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**Atomic-Scale Resolution Spectroscopy Applied to Thin-Film
Characterization**

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Introduction and Objectives

The objective of this program was to integrate atomic-resolution analytical techniques with more conventional methods of elemental, chemical, structural, and morphological characterization of surfaces, interfaces, and thin films in order to develop an ultimately better understanding of materials properties than could be obtained from each class of techniques by themselves. The emphasis was to develop methods for characterizing film growth, principally by chemical vapor deposition and sputter deposition. Applications are in electronic and magnetic thin films and nanostructures. The grant was primarily for the development of facilities. These include structural probes, optical probes, scanned probes, and probes of interface magnetic properties.

The facilities that were developed in this project divide into two categories: instrumentation that is commercially available and thus relatively easily implementable and very specialized equipment that we proposed to design and construct for novel applications. As a consequence the effort evolved at two rates: some instrumentation was in place within a year of the initiation of the grant. Some of the truly novel instrumentation was more difficult to implement and in some cases, its construction was delayed. We therefore requested a one-year no-cost extension to June 99, which was granted.

The goals and objectives did not change throughout the grant.

Accomplishments/New Findings

A. X-Ray Diffractometer

The new state-of-the-art x-ray diffractometer was operational within one year of grant initiation. It has been a workhorse in the research of a large number of groups. It has attracted new users because of its capabilities. It performs two major functions extremely well: thin-film and multilayer interface measurements and very-high-resolution double-crystal and reciprocal space mapping measurements of the crystallographic quality of thin films. Primary effort has been in the analysis of GaN films, SiGe/Si multilayers, materials for Al-free lasers, and SiGe, SiC, and GaN growth on compliant Si substrates. In addition the facility was used to test whether x-ray forward scattering can be used as a technique for in-situ real-time film roughness evolution measurements in CVD of SiGe films. The initial grant proposal specified that we would attempt to explore this possibility. The experiment showed that this approach was possible but that a stronger x ray generator would be better suited. This result has led to the initiation of a development effort, by Matyi, to create a focussing mirror arrangement for substantially increasing the flux from a conventional rotating source generator.

Kuech has used the machine for double crystal and reciprocal space mapping to develop GaN-related growth techniques. These materials were grown by both hydride vapor phase epitaxy and metal organic vapor phase epitaxy. The diffraction analysis was crucial in developing these materials efforts, which are supported by NSF and ONR funding. The measurements were essential in developing the first numerical fluid-thermal-chemical models of both HVPE and

MOVPE growth techniques. These models have determined the role of the local ammonia concentration in determining the crystal quality and defect (yellow) luminescence in these materials. Additionally, Kuech has used x-ray reflectivity to investigate the surface roughness of laser and quantum tunneling structures (resonant tunneling structures or RTDs) in an effort to correlate the measured interfacial and surface structure to device-level properties.

Botez has used the diffractometer in pioneering work on Al-free lasers at several wavelengths: 0.73 μ m, 0.78 μ m, 0.81 μ m, 0.895 μ m, and 0.98 μ m. Such lasers are more powerful and more reliable than standard AlGaAs semiconductor lasers. Noteworthy achievements are world-record output powers at 0.98 μ m (10.6 W CW and 14.3 quasi-CW) and at 0.81 μ m (6.1 W CW); and the realization of the first Al-free lasers at 0.73 μ m (for photodynamic therapy), at 0.78 μ m (for pumping Ho:YAG lasers for use in free-space communications and medicine), and at 0.895 μ m (for use in MRI with noble gases). The last application is especially exciting since it has about a million times more resolution than NMR, and thus will lead to a revolution in diagnostics via MRI (brain, blood, lungs etc.).

Lagally has used the diffractometer in analyzing multilayers of SiGe/Si in which self-organized arrays of "quantum-dot" structures are grown. These pyramidal structures exhibit photoluminescence that is strong and very narrow and persistent to 180K. X-ray diffraction is used to test for alloy composition, interface roughness, and layer thicknesses, and is thus used in support of the growth studies. In addition, Lagally has used the facility to investigate compliant-substrate effects in SOI and SiGe growth on SOI.

B. LEEM

The low-energy electron microscope (LEEM), purchased from IBM, has been operational since October 1996. LEEM represents an ideal bridge between nanoscale and mesoscopic-scale characterization. Three separate streams of experiments were undertaken and are continuing: 1) fundamental studies of SiGe quantum dot growth on Si(001) (initially with Prof John Bean, University of Virginia), 2) homoepitaxy of GaN using gas source MBE (with Prof Phil Cohen, University of Minnesota and with Kuech), and 3) growth of SiGe and SiC on compliant substrates (with Kuech).

The LEEM is intended as an extremely versatile tool. There are eight ports aimed directly at the sample. Typically, one of the six contains a lens to focus UV light so that the instrument can be used as a real-time photoemission electron microscope (PEEM), and another of the six contains a secondary-electron detector so that the microscope can be used as a scanning electron microscope (SEM). Others are intended as viewports for optical spectroscopies and for gas lines for gas-source MBE/CVD growth, which can be imaged in real time. The microscope, in addition to LEEM capabilities (both bright and dark field), can perform mirror electron microscopy (MEM) and LEED. Experiments can be done at any temperature from ambient to about 1300 °C. All of these capabilities, other than the optical spectroscopies, were functional already after the second year of the grant and have been used continuously since. A limitation in the PEEM has been noted: the photon energy obtainable from the Hg source is not sufficient to perform PEEM on wide-bandgap materials such as GaN.

Because incompatibility existed between some of these experiments, equipment development to make possible the performance of "incompatible" experiments became necessary. A second growth chamber was designed and has been implemented: one chamber is used for III-N studies, the other for Group IV studies. The studies operate in parallel: data analysis occupies the time each group is not on the instrument per se. Novel results have been obtained both on SiGe 3D island growth and on GaN surface structure. Several papers, primarily in Phys. Rev. Letters, have been published on the SiGe work. The GaN work has so far been less successful, as it is much more difficult. We have, however, found a new diffraction mode that occurs in the wurtzite structure that makes imaging of steps in GaN possible in a straightforward way.

Studies of compliant substrates (in particular SIMOX wafers and bonded wafers) have also been very successful. We have been able to determine the strain field of an individual dislocation generated at the Si-oxide interface in SOI. We have begun to make LEEM studies on patterned Si and SOI surfaces.

C. Energy Loss Spectroscopy in RHEED During CVD Growth

Part of the AFOSR grant was to design and build an electron energy loss spectrometer that interfaces with a specially designed RHEED system that allows us to monitor the evolution of the growth front in real time in a CVD system, operating at pressures typical for LPCVD. A unique spectrometer designed in collaboration with Staib Instruments and built by Staib was shipped in 1998. It is also compatible with CVD pressures. It was designed to perform electron energy loss measurements and Auger spectroscopy and to enhance and extend the capabilities of RHEED, by filtering the inelastic electrons out of the RHEED beams, allowing a true elastic diffraction analysis of the growth front, without the typical Kikuchi lines to confuse the interpretation. Dynamic measurements of the evolution of surface morphology should become much more reliable. The combination of RHEED/ELS is unprecedented in CVD growth. Unfortunately, the ELS has not worked as well as we had envisioned. There does not appear to be enough sensitivity to observe energy loss spectra of core level lines. Auger spectroscopy and plasmon loss spectroscopy have been demonstrated.

D. Surface Sum Frequency Generation Spectroscopy

A surface sum frequency generation spectroscopy capability intended for use both as a stand-alone system and to interface with CVD growth, LEEM, and STM was developed. The system, consisting of a Nd:YAG pulsed picosecond laser, an Optical Parametric Generation (OPG) stage, optical components, sample stage, detection optics, and electronics, has been installed and is functional, although we have had much difficulty with Continuum on components that they have routinely made for many years (and no difficulty on components that are specially made for us). The system has not been used as effectively as we had expected.

Initial experiments using this system to perform Surface Second Harmonic Generation (SSHG) spectroscopy of photoisomerization of an azobenzene surfactant at a liquid-liquid interface were completed. The experiments determined what fraction of a monolayer photoiso-

merizes from trans to cis. This work was done by Roberta Naujok, a student of Professor Robert Corn of the Chemistry Dept. Bobbie completed her Ph.D. dissertation and is now employed by 3M Company. Eugene Rudkevich assisted in setting up the facility and establishing the research program on surfaces described below. Eugene received his Ph.D. in Electrical Engineering and is now employed by HP.

Surface sum frequency generation spectroscopy experiments have not yet been performed, in part because of the difficulties we have had with Continuum and their laser products and in part because research interests have shifted.

E. Low-Temperature NSOM

An atmospheric-pressure NSOM and near-field photoreflectance microscope has been constructed by Kuech and is being tested. The instrument has a very high collection efficiency and thus a high sensitivity.

F. Instrumentation to Measure "Magnetic Roughness" of Interfaces in Multilayers

This grant also supports enhancement of a facility for performing unique measurements of magnetic properties of thin films, in particular the interface between magnetic and nonmagnetic materials. It has been speculated that giant magnetoresistance depends on the interface between magnetic and nonmagnetic material, in particular the nature of the "magnetic roughness" of the interface, but it has been difficult to prove this. Our unique x-ray scattering facility at the Synchrotron, a multilayer mirror beamline, allows us to make x-ray magnetic circular dichroism diffuse intensity measurements. To our knowledge, such measurements are not possible elsewhere.

The existence of this beam line and the success we have had in showing that we could make unique x-ray scattering measurements has allowed us to leverage the present grant to obtain additional funding from NSF to build a versatile new growth chamber at the synchrotron for simultaneous sputter deposition and evaporation, in-situ RHEED (using a system identical to the one described above), and several synchrotron radiation based magnetic measurements, by connecting this chamber, which is portable, to a number of different beam lines. New sputter sources were purchased for this chamber near the end of the grant period. Funds were also provided for updating the scattering chamber, including detectors. In addition to ours, several research groups, led by Franz Himpsel, Brian Tonner, two other users of the synchrotron not from the University of Wisconsin, and staff of the Synchrotron Radiation Center are participating in this effort. The AFOSR grant is therefore having a significant impact on the research of a number of researchers interested in magnetic thin films.

G. Carbon Nanotube Growth

The grant allowed us to initiate a program to fabricate carbon nanotubes in house, something that was not in the original proposal but which definitely has enhanced the goals of the grant. The purpose of this project was to develop carbon nanotube (CNT) probes for sur-

face metrology. This has been very successful, see below. A chamber for CNT growth was developed, with the additional goal to test the effect of ultrasonic agitation of electrodes on length and orientation of arc-grown CNTs. It has been possible to grow CNTs and to use these to fabricate probes for AFM. It has so far not been proven that ultrasonics has any effect, but these experiments are continuing.

H. Atomic Force Microscopy with Carbon Nanotube Tips

A commercial AFM was purchased as the foundation of the nanotube probe development, but also as a general-use instrument and as a development tool for faster AFMs. This AFM has been a complete success. Using it, we have developed carbon nanotube AFM probes that have much higher resolution and greater lifetime than conventional commercially available Si or Si nitride tips on cantilevers. We have transferred this technology so that now these nanotube AFM tips are commercially available. The AFM has been used continuously both with the nanotube probes and with conventional probes, by a large number of research groups for a variety of projects. These include a project to use CNTs as dip pens to load DNA into very small arrays, measurements (using the CNTs) of the surface granularity and roughness of magnetic thin films in a collaboration with a large magnetic data storage company, measurements of SiGe quantum dots with record spatial resolution, and measurements of amorphous oxide films sputter deposited on plastic films.

I. Upgrade of Scanning Auger Microscope and ESCA Facilities

In order to bring our surface analysis systems up to modern standards, we replaced the data acquisition and computing systems. These systems are used by a very wide variety of researchers. This investment in mesoscopic characterization techniques, in keeping with the goals of the grant, enhanced our total capability for thin-film characterization.

Personnel Directly Supported in this Grant Period

This list does not include users of the facilities who received no direct salary support from the grant. In all cases, the personnel below received only partial support from the grant.

Max G. Lagally	Seunghyun Baik (student)
Jim MacKay (postdoc)	Jenice Con Foo (postdoc)
Weiping Cai (student)	Rusi Debu (student)
Feng Liu (staff scientist)	Michael Meeks (student)
John Kelly (student)	Paul Rugheimer (student)
Adam Li (student)	Shaoping Wang (postdoc)
Nobuyoshi Kitamura (postdoc)	John Goomey (student)
Heather Evans (technician)	Xiaorong Qin (postdoc)
Dai Zhao (postdoc)	Eric Rehder (student)
Don Savage (staff scientist)	Katerina Moloni (postdoc)
Jeff Maxson (student)	Yuegang Zhao (student)
Eli Mateeva (postdoc)	Rich Matyi (faculty)

Amit Lal (faculty)
Jian Ma (postdoc)

Anthony Frutos (student)
Assaf Thon (postdoc)

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Interactions/Transitions

a. Presentations at meetings

Approximately 80 presentations or posters were given at national and international meetings on work supported by the facilities developed under this grant. Because of the multiple users of the facilities an exact count is not possible. At least 15 papers were invited. Conferences included APS, MRS, AVS, ACS, EMC, various international conferences - Japan, China, Taiwan, Canada, Germany, France, England, Greece, Italy, Finland, various workshops, and various specialty conferences.

b. Consultative and advisory functions

We calibrated optical blocking filters that will be used in soft-x-ray spectroscopy in space for an Astrophysics research group from Penn State (Prof. Gordon Garmire). They are part of a multimillion-dollar NASA sponsored project. The spatial map of transmission by these filters of soft x rays at a number of energies must be determined to better than 1%. The x-ray beam line that we use in our magnetic scattering turns out to be the only facility in the world capable of this level of calibration. As a consequence of the outstanding success we had in this calibration, we have been invited to participate in a prospective new NASA proposal to design and construct the x-ray optics for a new spectrometer.

The same beam line has also been used for novel soft x-ray radiation biology measurements. Using a lithographically fabricated mask, we have helped a group from Oncology and Medical Physics to create a spatially resolved (<5 micrometer) irradiation pattern in nuclei of individual cells. The spatially localized damage allows the biologists to investigate damage patterns and cell repair mechanisms. This is the first time such measurements have been possible. Again the precise doses and maintenance of the fidelity of the beam in our beam line makes these measurements possible.

We developed optical interference filters on plastic for a local company, via sputter deposition of metallic and metal-oxide multilayers.

c. Transitions

Carbon nanotube atomic force microscopy probes developed as described above are now commercially available through Piezomax Technologies, Inc., a Madison company. They have been purchased by researchers from a spectrum of establishments, including government labs, academia, and industry.

Al-free laser structures were developed by Mawst and Botez, using the x-ray facilities established with this grant. The success of these lasers in the lab has led to the formation of a new company, Alfalight, in Madison. The lasers to be developed will have major implications for the communications industry.

The work with Penn State described above has led to advanced filter capabilities and thus will aid the national research effort and probably lead to improved technology in these missions. The quantitative capability of our beamline makes it ideal for calibration of x-ray detectors, filters, and dosimeters in the soft-x-ray region of the electromagnetic spectrum.

New Discoveries

Al-free laser structures were developed by Mawst and Botez, using the x-ray facilities established with this grant.

A new x-ray scattering-based method for determining magnetic interface roughness was developed and proved. It has led to new research contracts from Seagate Technology, a magnetic data storage company.

A new LEEM method for analyzing steps at the surface of wurztite structures was discovered.

Honors/Awards

Lagally was elected to Leopoldina, the German National Academy of Sciences, in 1999. He also received the Outstanding Science Alumnus Award of the Pennsylvania State University in October 1996. He was the 1994 recipient of the MRS Medal, awarded by the Materials Research Society and the 1995 recipient of the Davisson-Germer Prize of the American Physical Society. The research supported by AFOSR is part of the body of work that was recognized by these awards.

University of Minnesota Subcontract (Prof. P.I. Cohen)

Accomplishments/New Findings

GaN was grown on bulk GaN samples using molecular beam epitaxy and compared to growth of GaN on sapphire. Source materials were provided by a Ga effusion cell and an ammonia leak. The surfaces were characterized during growth by reflection high-energy electron diffraction (RHEED), and then after growth by ultrahigh vacuum scanning tunneling microscopy

(STM) and atomic force microscopy (AFM) in air. Both surface polarizations were examined. This work shows what is possible for this difficult material even if the substrate problem were solved.

The GaN(0001)B surface of the bulk sample was polished by chemical and mechanical means, with a remaining rms roughness of a fraction of a nm. The GaN(0001)A surface of the bulk sample was only mechanically polished with a somewhat larger rms roughness and with remaining subsurface damage extending about 250 nm into the sample. Well ordered epitaxial growth could be obtained on the GaN(0001)B surface under a wide range of growth parameters. Smooth morphologies on the GaN(0001)A surface were obtained under conditions of excess Ga, near 850C.

Growth on a GaN(0001)B surface polished 2 deg toward the $\langle 1-2-20 \rangle$ under excess N and step flow conditions produced a well ordered step train. These surfaces exhibited a 1×1 diffraction pattern during growth. After growth and then cooling to room temperature in an ammonia flux, missing line defects were observed in STM that were perpendicular to the step edges and separated by about 2.5 nm. The structure similar to that identified by Packard and Dow as that due to heating GaN on sapphire to high temperature in the absence of a N source. The work presented here shows that the missing line structure is the N-rich reconstruction during growth.

On the chemo-mechanically polished face, the low temperature Ga rich reconstructions reported by Feenstra and coworkers were observed. At growth temperatures, only 1×1 diffraction patterns were observed. By contrast, the GaN(0001)A surface showed a weak 2×2 reconstruction at growth temperatures.

Growth on the GaN(0001)B surface was compared to growth on sapphire under a wide range of conditions. On the bulk samples, under comparable conditions, there was a lower hillock density. No pinholes were observed on the bulk samples. Two main growth limits were examined for low-index surfaces. First, under conditions of excess Ga, growth was generally smoother on both bulk and sapphire substrates than under N rich conditions. Hillocks were observed with meandering step edges. And after growth on the bulk samples, a mixture of $c/2$ and c height steps (where c is the height of a conventional cell) were observed. Second, under conditions of excess N, the bulk samples did not exhibit a strong tendency to 3D growth, unlike growth on sapphire. RHEED intensity oscillations, were observed that corresponded closely to growth of $c/2$ height monolayers of GaN, at lower ammonia fluxes. As the ammonia flux was increased, the period of growth increased. The period also increased with substrate temperature, with an activation energy that we identify with a surface diffusion process of 1.1 eV.

Using desorption mass spectroscopy we have applied the early kinetic methods developed by J.R. Arthur on GaAs to GaN. We have measured the desorbed Ga flux from a GaN surface upon the initiation and interruption of a Ga flux. The time dependence of the data can only be explained by a temperature dependent sticking coefficient of Ga.

The sublimation rate of GaN was measured as a function of the incident Ga and ammonia fluxes. If the rate is compared to a mass action analysis, good agreement is obtained only if about one half of the incident Ga sticks to the surface. This is currently being compared to the temperature dependent sticking coefficient found in the desorption mass spectroscopy work. This sublimation work also exhibits a change in surface morphology that has not previously been noted. We are attempting to measure the rate of sublimation vs crystallographic orientation.

A series of rate equations have been developed to describe the the adsorption/desorption processes that include a mean field description of surface diffusion. We are currently trying to extend these equations to cover the growth situation.

Finally, macrosteps have been observed on GaN B surfaces when growth is performed at lower temperatures and nearly 1:1 Ga to ammonia fluxes. Similar macrosteps have been observed on other III-V's such as GaAs(111) but they are as yet unexplained. Several mechanisms are possible, including a step instability and impurity pinning. However, which is responsible has not yet been determined. We are currently measuring their terrace length vs growth time and the role of the surface misorientation.

In short, we should soon have an understanding of the growth of GaN at a microscopic level that is comparable to our understanding of the growth of GaAs.

Personnel Supported

R. Held
B. Ishaug
P. I. Cohen

Publications

D. E. Crawford, R. Held, A. M. Johnston, A. M. Dabiran and P. I. Cohen, MRS Internet J. Nitride Semicond. Res., 1 (1996), "Growth rate reduction of GaN due to Ga surface accumulation"

R. Held, D. E. Crawford, A. M. Johnston, A. M. Dabiran and P. I. Cohen, J. Electron. Mater. (USA), 26, 272-80 (1997), "In situ control of GaN growth by molecular beam epitaxy."

R. Held, D. E. Crawford, A. M. Dabiran, A. Johnston, and P. I. Cohen, "N vs Ga limited growth of GaN," invited review, Surf. Review and Letters, August 1998.

A. M. Dabiran, S. M. Seutter and P. I. Cohen, "Direct observations of strain limited island growth of Sn doped GaAs(100)," Surf. Review and Letters, August 1998.

Interactions/Transitions

a. Presentations at meetings

"N vs Ga limited Growth", Physics and Chemistry of Semiconductor Interfaces, R. Held, D.E. Crawford, A. Dabiran, and P.I. Cohen, North Carolina, 1997.

"In-Situ studies of the growth of GaN on sapphire," (invited) U.S.-Japan Seminar on the Dynamics of Epitaxial Growth, Nagoya, Japan, March 1997.

"Homoepitaxial Growth of GaN", with R. Held, G. Nowak, S. Seutter, MRS, Fall, 1997.

"Surface diffusion on GaN," EGW conference, with R. Held and G. Nowak, Warsaw, Poland (1998)

"Growth Kinetics of GaN," with R. Held, G. Nowak, and A.M. Dabiran, spring MRS, 1999 (invited)

"Growth of GaN by MBE," PCSI 1999, invited.

b. Consultative and advisory functions

Continued discussions on the use of RHEED and desorption mass spectroscopy (DMS) for the growth of GaN and contacts to GaN have been underway with Dr. Joe Van Nostrand at Wright Laboratories.

Dave Look (Wright Laboratories) has examined several of samples grown at Minnesota using variable temperature Hall measurements. We are working together to determine differences in material quality caused by growth technique, i.e. MOCVD vs MBE.

c. Transitions

Using the technologies developed in the growth of GaN an STTR program was established with Silver Sky Technologies, Inc. (St. Paul) to evaluate lateral epitaxial overgrowth processes using MBE for the growth of high quality thin GaN films on sapphire.

GaN/sapphire samples have been provided to the University of Wisconsin for LEEM studies. Consultation on the use of ammonia in UHV systems has been provided.

Discoveries

Non-unity sticking coefficient of Ga on GaN.

Macrostep formation during the growth of GaN.

Honors/Awards

None